A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. VI.

By Tetsuya ISHIKAWA.

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In an earlier paper,[1] the writer reduced Dunstan and Wilson's equation connecting logarithms of the absolute viscosity and the molecular weight into a form:

$$\log\eta = -3.22 + bM$$

(where η and M are the viscosity coefficient and the molecular weight of a liquid, and b is a particular constant for the particular liquid, depending upon the temperature) and showed that the values of b and the field-constant k are practically the same when both are compared with those for benzene.

Other formulas showing the relation between the viscosity coefficient and the molecular weight have been proposed by Gartenmeister[2] and Macleod.[3]

Gartenmeister deduced the following relation from his careful determinations of the absolute viscosity of various liquids:

$$\eta = k_G M, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where k_G is a particular constant within the observed temperature range for chlorine, bromine and iodine substitution compounds.

For those which do not obey the rule such as homologous series in which successive members differ by CH_2, he took M^2 in place of M, but the constancy of their proportional constants are not satisfactory.

Macleod, having drawn attention to the fact that the relation between the viscosity of liquids and their coefficients of expansions and densities can be explained on the assumption that the viscosity is a simple function of the free space within the liquid, proposed the expression:

$$\eta_t x_t^A = C,$$

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(1) This Bulletin, **4** (1929), 149.
(2) R. Gartenmeister, *Z. physik. Chem.*, **6** (1890), 524.
(3) D. B. Macleod, *Trans. Faraday Soc.*, **19** (1923), 6; **21** (1925), 145 and 151.

where η_t is the viscosity at a temperature t, x_t the free space at that temperature, C is a constant for the particular liquid, and A is approximately unity for unassociated substances. In this calculation he assumed that the expansion is wholly confined to the free space and the volume of the molecules remains constant, and put

$$x_t = x_0 + \frac{v_t}{v_0} - 1,$$

in which x_0 is the free space at 0°; v_t and v_0 are the specific volumes at $t°$ and 0° respectively.

Macleod further observed that by putting A as unity (which causes no serious error in finding x_0 for normal liquids) C is proportional to the molecular weight. He applied this method of calculation to any liquid, in this case, however, the discrepancy of the proportional constant from the value obtained for such a normal liquid as octane he attributed to the molecular complexity of the liquid and put forward the expression :

$$\eta = \frac{k_M a_M}{x}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where a is the degree of association and k_M is a constant for all liquids.

Comparing the equal terms in expressions (1) and (2), we get

$$k_G x = k_M a$$

With the object of testing which of the values k_G or $k_G\, x$ gives more constancy, the present writer will make use of the values at 0°C. tabulated by Macleod in his paper.[1]

Table 1.

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot k_G \cdot x_0$
C_2H_5Br	0·00478	109·0	0·1080	4·39	4·74
C_3H_7Br	0·00645	123·0	0·0908	5·24	4·76
i-C_3H_7Br	0·006045	123·0	0·0923	4·92	4·54
i-C_4H_9Br	0·008235	137·0	0·0829	6·01	4·98
CH_3I	0·005945	142·0	0·0967	4·19	4·05
C_2H_5I	0·00719	156·0	0·0907	4·61	4·18
C_3H_7I	0·00938	170·0	0·0782	5·52	4·31
i-C_3H_7I	0·008785	170·0	0·0836	5·17	4·32

(1) D. B. Macleod, *Trans. Faraday Soc.*, **21** (1925), 154–155.

Table 1.—(*Continued*)

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot x_0$
C_5H_{12}	0·00283	72·1	0·1207	3·93	4·74
i-C_5H_{12}	0·00273	72·1	0·1202	3·79	4·55
C_6H_{14}	0·003965	86·1	0·0979	4·60	4·51
i-C_6H_{14}	0·00371	86·1	0·1054	4·31	4·54
C_7H_{16}	0·00519	100·1	0·0863	5·19	4·48
i-C_7H_{16}	0·00477	100·1	0·0883	4·77	4·21
C_8H_{18}	0·00703	114.1	0·0744	6·16	4·58
CH_3OH	0·00813	32·0	0·0580	25·4	14·7
C_2H_5OH	0·01770	46·0	0·0450	38·5	17·3
C_3H_7OH	0·03882	60·0	0·0233	64·7	15·1
i-C_3H_7OH	0·04564	60·0	0·0252	76·0	19·1
C_4H_9OH	0·05185	74·0	0·0248	70·0	17·4
i-C_4H_9OH	0·08038	74·0	0·0243	108·6	26·4
$HCOO{\cdot}CH_3$	0·00429	60·0	0·0994	7·15	7·11
$HCOO{\cdot}C_2H_5$	0·00505	74·0	0·0936	6·83	6·39
$HCOO{\cdot}C_3H_7$	0·00668	88·0	0·0768	7·59	5·83
$CH_3CO_2{\cdot}CH_3$	0·00478	74·0	0·0974	6·46	6·29
$CH_3CO_2{\cdot}C_2H_5$	0·00578	88·0	0·0820	6·57	5·39
$CH_3CO_2{\cdot}C_3H_7$	0·00770	102·0	0·0700	7.55	5·28
$H{\cdot}COOH$	0·02245	46·0	0·0356	48·8	17·4
$CH_3{\cdot}COOH$	0·01219	60·0	0·0564	20·3	11·5
$CH_3{\cdot}CH_2{\cdot}COOH$	0·01519	74·0	0·0563	20·5	11·5
$CH_3(CH_2)_2{\cdot}COOH$	0·02284	88·0	0·0417	26·0	10·8
$(CH_3)CH{\cdot}COOH$	0·01885	88·0	0·0463	21·4	9·92
$CH_3{\cdot}CO{\cdot}CH_3$	0·00394	58·0	0·1134	6·79	7·70
$C_2H_5{\cdot}CO{\cdot}CH_3$	0·005385	72·0	0·0827	7·48	6·19
$C_2H_5{\cdot}CO{\cdot}C_2H_5$	0·00595	86·1	0·0800	6·91	5·53
$C_3H_7{\cdot}CO{\cdot}CH_3$	0.00644	86·1	0·0754	7·48	5·64
C_6H_6	0·009025	78·0	0·0585	11·6	6·77
$C_6H_5CH_3$	0·007685	92·0	0·0642	8·35	5·36
$C_6H_5C_2H_5$	0·00874	106·0	0·0545	8·24	4·49
o-$C_6H_4(CH_3)_2$	0·011025	106·0	0·0486	10·4	5·06
m-$C_6H_4(CH_3)_2$	0·00802	106·0	0·0597	7·57	4·52

Table 1.—(*Continued*)

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot k_G \cdot x_0$
CS_2	0·004295	76·0	0·1206	5·65	6·81
$(CH_3)_2S$	0·00354	62·0	0·1150	5·71	6·57
$(C_2H_5)_2S$	0·00559	90·0	0·0863	6·21	5·36
$C_2H_5 \cdot O \cdot C_2H_5$	0·00286	74·1	0·1234	3·86	4·76
$C_3H_7 \cdot O \cdot CH_3$	0·00307	74·1	0·1272	4·14	4·86
$C_3H_7 \cdot O \cdot C_2H_5$	0·003965	88·0	0·0994	4·50	4·48
$C_3H_7 \cdot O \cdot C_3H_7$	0·00540	102·0	0·0816	5·29	4·32
$i\text{-}C_4H_9 \cdot O \cdot CH_3$	0·00381	88·0	0·1018	4·33	4·41
$i\text{-}C_4H_9 \cdot O \cdot C_2H_5$	0·00482	102·0	0·0887	4·73	4·19

It is easily understood from the above table that Gartenmeister's exceptional cases, to which homologous series such as alcohols and acids belong, are sufficiently expressed by the formula $\eta=KM$, K being corrected for Macleod's free space and that for some substitution compounds such as formates and ketones more constancy of the values of the proportional constants is obtained by Gartenmeister's formula than by Macleod's. In short, it being difficult to justify which is the superior of the two so far as the present data are concerned, it seems highly probable, in accordance with the physical meaning that the viscosity is due to a transport of momentum, (i) that the viscosity η is proportional to the molecular weight M and (ii) that the proportional constant K in the expression $\eta=KM$ is a particular constant which plays a very important part.

Brillouin,[1] who made a success to interpret the negative temperature coefficient of viscosity of liquids from a theoretical standpoint of view, assumed that in liquids where the molecules are continually in collision and where the transfer of matter (diffusion) is ordinarily insignificant, when a molecule strikes all of the molecules in the vicinity are shaken and an elastic wave is found which is propagated through the medium, or, in other words, the molecules of liquids are never free and always under strong forces.

This intensity of attraction field must of course be taken into consideration in studying the viscosity of liquids. If the viscosity of a liquid is stoichiometrically related with the molecular weight as in the expression :

$$\eta=KM$$

(1) L. Brillouin, *J. phys. radium* [6] **3** (1922), 326 and 362.

the factor depending on the intensity of attraction field may be included in no other than the constant K.

According to Macleod's idea the constant K depends on the free space and the relative value K of a liquid to K of octane is simply equal to the degree of association of the liquid, for which, however as stated above, his deduction formula $\eta\, x = \text{const.}$ (x being the free space) does not hold true.

For a further test the comparison among the particular constants at 0°C. (relative to those for benzene) calculated from the three formulas of Dunstan and Wilson, of Gartenmeister and of Macleod will be made in the following.

Table 2.

Substance	$\frac{(b)C_6H_6}{b}$	$\frac{(k_G)C_6H_6}{k_G}$	$\frac{(k_G \cdot x)C_6H_6}{k_G \cdot x}$
C_6H_6	1	1	1
$C_6H_5CH_3$	1·25	1·39	1·26
$CH_3CO_2C_2H_5$	1·35	1·76	1·26
$CHCl_3$	1·69	1·98	1·22
CCl_4	1·72	1·32	1·29
CS_2	1·34	2·05	0·99
CH_3OH	0·43	0·46	0·46
C_2H_5OH	0·47	0·30	0·39
H_2O	0·18	0·12	0·33
CH_3COOH	0·69	0·57	0·59

Though a quite satisfactory coincidence among the constants may not be hoped for, yet it is probable that they are the equivalent quantities with one another and are consequently the corresponding factors with the writer's field-constant k.[1] Similar consideration as above shown, if it extends to binary mixtures, accords with the writer's theory.[2]

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(1) This Bulletin, **4** (1929), 149.
(2) This Rulletin, **4** (1929), 5.

COLLOIDAL SYNTHESIS OF CERTAIN READILY CRYSTALLIZABLE ORGANIC COMPOUNDS.[1]

By Nadine von WEIMARN.

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Compounds Studied up to the Present. The Methods of Preparation of their Colloidal Solutions.

The colloidal synthesis of those organic compounds, which are obtained under ordinary conditions in crystals clearly seen by the naked eye, has not been extensively studied.[2]

Below are summed up the general results of the colloidal synthesis of eight organic compounds (naphthalene, papaverine, camphor, salol, benzophenone, anthracene, anthraquinone and phenanthrene). In the near future the list will be enlarged.

Two methods of colloidal synthesis were employed: A. The cooling of a solution.[3] B. The replacing of one dispersion medium by another.[4]

General Results.

1. The first of the above five organic compounds give *stable* colloidal solutions only at *low* temperatures (e.g.–80°C.), in dispersion media consisting of concentrated (e.g. 68 per cent.) aqueous sucrose solutions congealed to glasses.

2. Colloidal anthracene solutions stable for not less than several months, are easily obtained e.g. by pouring into large volumes (99–495 c.c.) of distilled water of room temperatures, from one to several c.c. of alcoholic anthracene solutions (0.005–0.25 per cent).

3. Colloidal anthraquinone solutions obtained by pouring its alcoholic solutions into distilled water of room temperatures, are less stable than colloidal anthracene solutions. Colloidal phenanthrene solutions are very unstable at room temperatures, owing to the greater solubility of phenanthrene in water. Colloidal solutions of anthraquinone and phenanthrene of a markedly longer stability may be obtained at low temperatures, at about

(1) For more details, see *Kolloid-Z.*, **50–51** (1930), 164 etc.
(2) P. P. von Weimarn, "Die Allgemeinheit des Kolloidzustandes," I (1925), 228.
(3) P. P. von Weimarn, "Grundzüge der Dispersoidchemie," (1911), 69.
(4) P. P. von Weimarn, "Grundzüge der Dispersoidchemie," (1911), 67.

0°C. or lower, with water or weak aqueous sucrose solutions as dispersion media.

4. Anthracene and phenanthrene readily form disperse systems, the particles of the disperse phases of which are not three-dimensionally colloid, as is usual, but *monodimensionally* colloid, because the lengths and breadths of the disperse particles, crystalline lamellae, are of microscopical dimensions. Anthraquinone gives easily disperse systems, the disperse particles of which are *bidimensionally* colloid. The lengths of the disperse particles, crystalline needles, considerably exceed the ultramicroscopic size. The structure of these disperse particles was defined by ultramicroscopical observations of P.P. von Weimarn.

5. Micro-and ultramicroscopic observations by P.P. von Weimarn on benzophenone and salol disperse systems, obtained at room temperatures, have shown that these disperse systems, in the first stage of their existence, are emulsoids or emulsions ; later on they pass into suspensoids and suspensions. These observations can be generalized for the colloidal systems of other organic substances with relatively low melting points.

I wish to express here my gratitude to my husband, Prof. Dr. P.P. von Weimarn for suggesting the theme of this investigation as well as for his guidance and help in every way during the work.

My acknowledgements are due also to Dr. Eng. I. Shoji, President of the Imperial Industrial Research Institute of Osaka.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART I.

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Introduction. One of the authors[1] had studied the oxidation velocities of sodium sulphite, stannous hydroxide and ferrous hydroxide in alkaline or in acidic solutions by means of air and found that the observed velocities

(1) S. Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **2** (1927) 259; **3** (1928), 76; **3** (1928), 137; **4** (1929), 48. *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40; **7** (1927), 189; **8** (1928), 93; **8** (1928), 230; **9** (1928), 203; **10** (1929), 7.

were independent of the concentrations of these oxidizable substances under the conditions of the author's experiments. The results were interpreted by the consideration that the dissolution velocity of oxygen is much slower than the true reaction velocity and the observed value will mean the dissolution velocity of oxygen into the liquid.

The phenomenon is a special case of the heterogeneous reaction between gaseous and liquid phases and the mechanism can be explained by the following considerations.

The difference between the number of molecules of a gas which enter into the liquid phase and the number of molecules of the gas which leave the liquid phase through definite boundary surface area per unit of time can be called the dissolution velocity of the gas into the liquid at the given temperature and pressure. It is evident that the dissolution velocity of a gas into a liquid depends upon the partial pressure of the gas and the nature of the boundary surface. We can then expect that the dissolution velocity of a gas into a given liquid at the given temperature and pressure will have a maximum value when the concentration of the gas in the boundary surface is kept zero.

This state can be maintained if the sufficient quantity of a substance be present in the surface layer to react with all of the molecules of the gas which enter into the liquid phase per unit of time. Under this condition, the dissolution velocity of the gas will be independent of the concentration of the reacting substances, if the presence of the necessary quantity of the latter in the surface have not much effect upon the nature of the boundary surface. The reaction velocity of the substance with the gas will also be maximum under this condition, and it can not increase however its concentration is increased, as the reaction velocity with the gas can not be greater than the maximum dissolution velocity of the gas into the liquid.

The phenomenon is in some degree analogous to that of the saturation current conducted by electrons emitted by a heated body in an electric field. The current can not be greater than a definite value however the strength of the field is increased, if the temperature of the heated body be kept constant.

Under the conditions of the present research, the oxidation velocity of sodium sulphite solution by means of air is independent of its concentrations. According to the viewpoint, above described, the result should mean the maximum reaction velocity of the solution with air at the given temperature, and the dissolution velocity of oxygen into water, obtained from the result, should mean the maximum dissolution velocity of oxygen into water at the given temperature and pressure.

Mitsukuri[1] has explained the dissolution velocity of carbon dioxide into sodium hydroxide solution by the consideration that the reaction takes place in the thin liquid surface layer. The result of this investigation will also be able to interprete by Mitsukuri's theory, if we only consider the thickness of the diffusion layer of oxygen is extremely small and the concentration of the reacting substance is sufficiently great. It will be impossible to decide whether it is necessary to assume the existence of the liquid film at the surface in order to interprete the present results.

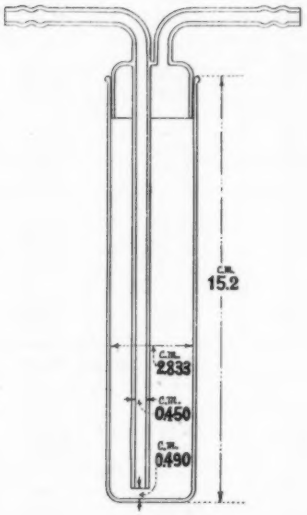

Fig. 1

Experimental. The oxidation velocities of sodium sulphite solution were observed when air is passed at various velocities. The experimental procedure is quite the same as that described in the previous papers.[2] The reacting vessel employed is shown in Fig. 1. Air, washed by acidified potassium bichromate solution and alkali, was passed at uniform velocity into the solution of sodium sulphite of known concentration, the total volume of the solution being made to 40 c.c. in each case. After t-minutes, the air current was stopped and the total quantity of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back by means of sodium thiosulphate solution, v in the following tables, being the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite.

The values of k are calculated by $k=\frac{1}{t-t_0}(v_0-v)$, v_0 being the value of v at $t=t_0$. The values of $v_{calc.}$ given in the tables were obtained by the equation $v_{calc.}=v_0-k\,(t-t_0)$, using the mean value of k.

(1) S. Mitsukuri, *The Science Reports of the Tohoku Imperial University*, Series 1, Vol. 18, No. 2. (June 1929).

(2) Loc. cit.

Table 1.

Temp. = 25°C.

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
30.5	3	19.83	—	—
	23	17.54	17.63	0.115
	43	15.21	15.43	0.116
	3	27.71	—	—
	23	25.39	25.51	0.116
	43	23.31	23.31	0.110
	3	33.68	—	—
	24	31.21	31.37	0.118
	43	29.17	29.28	0.113
	3	38.32	—	—
	23	36.10	36.12	0.111
	43	34.01	33.92	0.108
	3	47.50	—	—
	21	45.65	45.52	0.103
	41	43.39	43.32	0.108
	3	52.37	—	—
	23	50.49	50.17	0.094
	43	48.19	47.97	0.105
			Mean	0.110
60.3	3	19.45	—	—
	23	16.23	16.11	0.161
	43	12.99	12.77	0.162
	3	27.58	—	—
	23	24.24	24.24	0.167
	43	20.97	20.90	0.165
	3	34.49	—	—
	23	31.01	31.15	0.174
	43	27.67	27.81	0.171
	3	40.66	—	—
	23	37.14	37.32	0.176
	43	33.83	33.98	0.171
	3	47.60	—	—
	23	44.24	44.26	0.168
	43	41.11	40.92	0.162
	3	54.03	—	—
	23	50.80	50.69	0.162
	43	47.42	47.35	0.165
			Mean	0.167

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v. c c.	$v_{calc.}$ c.c.	k.
86.7	3	16.32	—	—
	23	12.24	12.14	0.204
	43	7.49	7.96	0.221
	3	17.66	—	—
	43	9.16	9.30	0.213
	3	18.89	—	—
	23	14.95	14.71	0.197
	43	9.91	10.53	0.225
	3	20.01	—	—
	23	15.76	15.83	0.213
	43	11.70	11.65	0.208
	3	23.82	—	—
	23	19.82	19.64	0.200
	43	15.40	15.46	0.210
	3	26.53	—	—
	23	22.27	22.35	0.213
	43	18.62	18.17	0.198
	3	27.52	—	—
	23	23.59	23.34	0.197
	43	19.25	19.16	0.202
	3	30.21	—	—
	23	26.06	26.03	0.208
	43	22.18	21.85	0.202
	3	33.21	—	—
	23	28.95	29.03	0.213
	43	24.58	24.85	0.216
	3	33.68	—	—
	7	32.84	32.84	0.210
	28	28.21	28.45	0.219
	3	41.46	—	—
	23	37.68	37.28	0.189
	43	33.18	33.10	0.207
	3	46.60	—	—
	23	42.27	42.42	0.217
	43	38.01	38.24	0.215
	3	51.26	—	—
	23	46.99	47.08	0.214
	44	42.20	42.69	0.221
			Mean	0.209

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
111.7	3	16.60	—	—
	23	11.77	11.58	0.242
	43	7.07	6.58	0.238
	3	18.91	—	—
	23	14.11	13.89	0.240
	43	8.49	8 87	0.261
	3	22.20	—	—
	43	12.57	12.16	0.241
	3	22.58	—	—
	23	17.43	17.56	0.258
	43	12.20	12.54	0.260
	3	24.82	—	—
	23	19.80	19.80	0.251
	43	14.27	14.78	0.264
	3	28.64	—	—
	23	23.78	23.62	0.243
	43	18.47	18.60	0.254
	3	28.87	—	—
	23	24.04	23.85	0.242
	43	18.40	18.83	0.262
	3	32.70	—	—
	23	27.77	27.68	0.247
	43	21.98	22.66	0.268
	3	40.01	—	—
	23	35.06	34.99	0.248
	43	30.00	29.97	0.250
			Mean	0.251
137.0	3	20.90	—	—
	43	8.54	9.06	0.309
	3	23.00	—	—
	23	17.16	17.08	0.292
	43	11.87	11.16	0.278
	3	31.01	—	—
	23	24.95	25.09	0.303
	43	18.48	19.17	0.313
	3	35.16	—	—
	23	29.40	29.24	0.288
	43	23.70	23.32	0.287
	3	39.77	—	—
	43	28.16	27.93	0.290
	3	44.93	—	—
	43	33.29	33.09	0.291
	3	45.13	—	—
	23	39.25	39.21	0.294
	43	33.07	33.29	0.302
	3	52.15	—	—
	23	46.22	46.23	0.297
	43	40.37	40.31	0.295
	3	58.72	—	—
	23.5	52.58	52.65	0.300
	43.5	46.52	46.73	0.301
			Mean	0.296

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
160.8	3	21.80	—	—
	43	8.34	8.48	0.337
	3	22.50	—	—
	23	16.19	15.84	0.316
	43	9.90	9.18	0.315
	3	31.17	—	—
	23	24.61	24.51	0.328
	43	17.69	17.85	0.337
	3	33.43	—	—
	43	20.41	20.11	0.326
	3	38.75	—	—
	23	32.29	32.09	0.323
	43	24.89	25.43	0.347
	3	43.33	—	—
	43	29.97	30.01	0.334
	3	45.51	—	—
	23	38.75	38.85	0.338
	43	32.13	32.19	0.335
	3	55.96	—	—
	23	49.17	49.30	0.340
	43	42.46	42.64	0.338
	3	57.22	—	—
	42	43.44	44.23	0.353
			Mean	0.333
182.8	3	31.29	—	—
	43	17.07	17.01	0.356
	3	31.67	—	—
	43	17.30	17.39	0.359
	3	52.78	—	—
	43	38.80	38.50	0.350
	3	58.22	—	—
	43	43.51	43.94	0.368
	3	68.88	—	—
	43	54.72	54.60	0.354
			Mean	0.357

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
201.8	3	34.20	—	—
	23	26.40	26.22	0.390
	43	17.77	18.24	0.411
	3	42.41	—	—
	43	26.09	26.45	0.408
	3	45.65	—	—
	23	37.85	37.67	0.390
	43	29.82	29.69	0.396
	3	45.76	—	—
	43	29.72	29.80	0.401
	3	50.26	—	—
	23	42.12	42.28	0.407
	43	34.51	34.30	0.394
	3	50.94	—	—
	43	34.36	34.98	0.415
	3	58.41	—	—
	23	50.64	50.44	0.389
	43	42.17	42.46	0.406
	3	66.93	—	—
	43	51.66	50.97	0.382
				Mean 0.399

Table 2.

Temp.=25°C.

V (Velocity of air) c.c./min.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles/min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles/min.
30.5	0.110	0.115	2.75×10^{-6}	2.89×10^{-6}
60.3	0.167	0.165	4.18 ,,	4.12 ,,
86.7	0.209	0.208	5.23 ,,	5.20 ,,
111.7	0.251	0.249	6.28 ,,	6.23 ,,
137.0	0.296	0.291	7.40 ,,	7.28 ,,
160.8	0.333	0.330	8.33 ,,	8.26 ,,
182.8	0.357	0.366	8.93 ,,	9.16 ,,
201.8	0.399	0.398	9.98 ,,	9.95 ,,

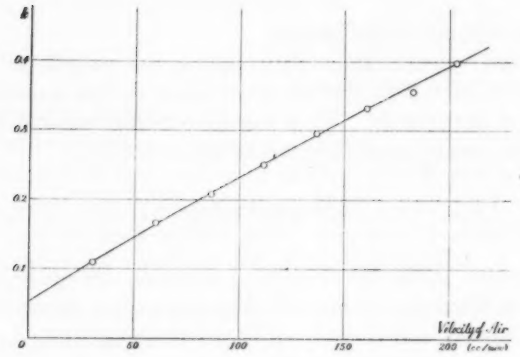

Fig. 2.

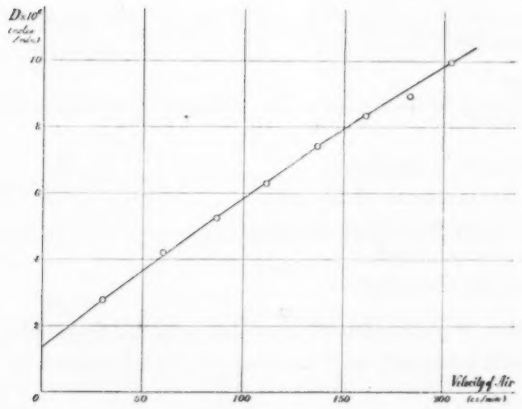

Fig. 3.

The oxidation velocity observed is thus independent of the concentration of sodium sulphite. According to the viewpoint above described, the observed value is the maximum oxidation velocity of sodium sulphite by means of air.

From the results it can be seen that the velocity constant is a linear function of the velocity of air passed, as is shown graphically in Fig. 2. The values of $k_{calc.}$ given in the third column of Table 2, were calculated by

$$k_{calc.}=0.001648V+0.0652 \quad \ldots\ldots (1)$$

where V is the velocity of air passed.

The observed velocity constant k means the volume of sodium thiosulphate solution of 0.1000 normal equivalent to the amount of sodium sulphite oxidized per minute. Then the dissolution velocity of oxygen into water under this special condition can be expressed by

$$D_{obs.}=\frac{1}{4}k_{obs.}\times 10^{-4} \text{ moles per minute.} \quad \ldots\ldots (2)$$

The calculated values of D by this equation are given as $D_{obs.}$ in the fourth column of Table 2. It is evident that $D_{obs.}$ is a linear function of the velocity of air passed in this case. It is shown graphically in Fig. 3. The values of $D_{calc.}$ given in the last column of Table 2 are those calculated by

$$D_{calc.}=4.121\times 10^{-8}V+1.630\times 10^{-6} \quad \ldots\ldots (3)$$

Theoretical. According to the kinetic theory of gases, total number of molecules which collide with unit boundary surface area per unit of time can be expressed by

$$\frac{NP}{\sqrt{2\pi MRT}} \quad \ldots\ldots (4)$$

where N=Avogadro's constant,
P=partial pressure of the gas,
M=molecular weight of the gas,
R=the gas constant,
T=absolute temperature.

Total number of molecules which enter into the liquid phase per unit of time through unit boundary surface area can be expressed by

$$\frac{\alpha NP}{\sqrt{2\pi MRT}} \quad \ldots\ldots (5)$$

where α is a quantity which depends upon the nature of the gas and the liquid and the partial pressure of the gas. With regard to one liquid, in the surface of which the concentration of the gas is kept zero, α may be represented by

$$\alpha=f(P) \quad \ldots\ldots (6)$$

Under this condition α may be taken to be constant if the partial pressure of the gas be constant.

The total boundary surface area which is in contact with the gas can be represented in the present experiment by

$$4\pi r^2 n\frac{l}{u}+s_0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where r=radius of a bubble,
n=number of bubbles passed per second,
l=the depth of the center of a bubble when it just leaves the exit,
u=the ascending velocity of the bubble,
s_0=the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

From (5) and (7) we can represent the total number of molecules which enter into the liquid phase per second by

$$\frac{aNP}{\sqrt{2\pi MRT}}\left(4\pi r^2 n\frac{l}{u}+s_0\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

The dissolution velocity of the gas can then be represented by

$$D=\frac{60aP}{\sqrt{2\pi MRT}}\left(4\pi r^2 n\frac{l}{u}+s_0\right) \text{ moles per minute.} \quad \ldots\ldots\ldots \quad (9)$$

when the concentration of the gas in the surface layer is kept zero.

Now,

$$n=\frac{1}{60}\frac{V}{\frac{4}{3}\pi r^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

see errata V.6, P.364

where V denotes the volume of the gas passed per minute.

Then,

$$D=\frac{60aP}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \text{ moles per minute.} \quad \ldots\ldots\ldots \quad (11)$$

Under the conditions of this research, the dissolution velocity of oxygen should be regarded as the maximum value, and the value of a can be considered to have a definite maximum value. As the values of P, T, r, and u are constant, from the equation (11) we have,

$$D=AV+B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

where A and B are constants.

see errata V.6, P.364

From (2) and (11) we have,

$$k=\frac{24aP\times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

Under the present conditions,

$$k=A'V+B' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

where A' and B' are constants.

The equations (12) and (14) are in good agreement with the experimental facts, above described.

The calculation of the values of α and s_0. The value of α in the above equations depends upon the condition of the boundary surface and the partial pressure of the gas. If the concentration of the gas in the surface layer be kept zero, α will have a definite specific value with regard to the liquid and gas. From the present experimental results we can calculate the maximum value of α concerning water and oxygen, whose partial pressure is 15.96 cm. Hg.

From the equations (3) and (11) we obtain,

$$\frac{3\alpha Pl}{r\,u\sqrt{2\pi MRT}}=4.121\times10^{-8} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

If we know the values of l, r, and u we can calculate the value of α from the equation (15).

The value of r was obtained by the following process. Air was passed into the reacting vessel from a gas burette at uniform velocity. From the volume of air passed, we can calculate the radius of one bubble by counting the number of bubbles. A slight difference of the radius of the bubble was observed, when we change the velocity of air passed. The mean value of the radius of a bubble was found to be 0.334 cm. when the mean value of the velocity of air passed is about 19.64 c.c. per minute. This value was employed for the calculation as an approximate value of the radius of a bubble.

According to the study on the motion of an air bubble rising in water by O. Miyagi,[1] the ascending velocity of an air bubble attains an uniform value almost immediately when it leaves the exit, and the ascending velocity is 23.1 cm. per second when the radius of the bubble is 0.334 cm. As the viscosity of sodium sulphite solution of such concentration as that employed in the present research is not much different from that of pure water, it can be expected that the ascending velocity of the air bubble in the solution will nearly be the same as that in pure water. The value 23.1 cm. per second was employed as an approximate value of u in the following calculations.

The value of l was observed directly to be 6.20 cm.

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(1) *Phil. Mag.*, **50** (1925), 112.

By introducing these values in the equation (15) we have,

$$\alpha=\frac{4.121\times10^{-8}\,r\,u\sqrt{2\pi MRT}}{3Pl}=1.794\times10^{-7}$$

This value means the ratio of the total number of the molecules of oxygen which enter into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time when the partial pressure of oxygen is about 0.21 atmosphere, the concentration of oxygen in the surface being maintained to be zero. The obtained value of α is the definite specific value with regard to water and oxygen at the given temperature and pressure.

The present chemical method will be able to employ in order to calculate the value of α with regard to various liquids and gases.

From the equations (3) and (11) we have,

$$\frac{60\alpha P}{\sqrt{2\pi MRT}}s_0=1.630\times10^{-6}$$

By introducing the value of α above obtained,

$$s_0=1.59\text{ cm.}^2$$

The calculated value of s_0 from Fig. 1 is about 5 cm.^{2} It is not curious that the calculated value of s_0 is much smaller than this value, for the most part of the upper surface of the liquid is occupied by the surface of the bubbles passed incessantly.

Summary.

(1) The oxidation velocity of sodium sulphite solution was observed when air is passed at various velocities.

(2) It was found that the oxidation velocities are independent of the concentration of sodium sulphite and the velocity constant was expressed as a linear function of the velocity of air passed.

(3) The dissolution velocity of oxygen into water when the concentration of oxygen in the surface layer is kept zero, was calculated from the obserbed reaction velocity, and it was found to be expressed as a linear function of the velocity of air passed.

(4) An interpretation of the mechanism of this reaction under the observed conditions was given.

(5) The maximum value of the ratio of the total number of molecules of oxygen which enter into water to the total number of molecules of oxygen which collide with the unit boundary surface per unit of time at 25° C. was calculated from the observed results.

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ON THE THERMAL DECOMPOSITION OF CRESOLS.

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It is a well known fact that the constituents of coal tar vary with the conditions under which coal is treated; the tar obtained from coals by low temperature carbonisation contains much cresol and no phenol nor benzene or merely traces, while the tar produced by high temperature distillation has less cresol but much phenol, benzene and toluene.[1] These facts suggest that at a high temperature, cresol should decompose into benzene, toluene and phenol as illustrated in the following scheme:

$$C_6H_4CH_3OH \rightarrow \begin{cases} C_6H_5OH + CH_3 & \text{demethylation} \quad (1) \\ C_6H_5CH_3 + H_2O & \text{dehydration} \quad (2) \\ C_6H_6 + H_2O + CH_3 & \text{dehydration \& demethylation} \quad (3) \end{cases}$$

On referring to the literature on the present subject, we noticed that J. Kraemer[2] has confirmed phenol by passing it through a glass or iron tube heated to a red heat, and it was decomposed into benzene and higher aromatic hydrocarbons. The removal of oxygen from phenol was also noted by W. Smith,[3] when phenol or cresol was introduced into a glowing glass tube, filled with charcoal or iron filings, a small amount of benzene or toluene was produced together with a large amount of gaseous substances. On bringing phenol vapour into contact with a heated platinum wire, H.

(1) A. Warnes, "Coal tar distillation" (1923), 65; C. Lander and R. MacKay, "Low temperature carbonisation" (1924), 71, 79; H. Strache und R. Lant, "Kohlenchemie" (1924), 381; F. Wirth, "Brennstoff Chemie" (1926), 396.

(2) J. Kraemer, *Ann.*, **189** (1877), 129.

(3) W. Smith, *J. Soc. Chem. Ind.* **9** (1890), 447.

Meyer[1] has identified benzene in the reaction product. Demethylation of cresol was reported by F. Fischer[2]; according to his report, cresol vapour passed with hydrogen or carbon monoxide through a tube heated to 700°–800°C., yields phenol as well as benzene. E. Müller[3] has reported that cresol, when passed through an iron tube heated to 700°–800°C., was found to decompose chiefly into methane, carbon monoxide, hydrogen and carbon, and a small amount of benzene and tarry matter were also produced, and that the proportion of the chief reaction products is as follows:

$$C_6H_4CH_3OH \longrightarrow CO+CH_4+2H_2+5C.$$

1. The Thermal Decomposition of *m*-Cresol. The writer's supposition for the thermal decomposition of the cresol, which was mentioned above, was partly confirmed by the experiments of many investigators in subjecting phenol to a high temperature with or without catalysts. However, the mechanism and conditions for the formation of benzene, toluene and phenol from cresol remained in a state of uncertainty. The present research was undertaken with the intention of obtaining confirmation of the true nature of the pyrogenic decomposition of cresols and also to settle the conditions under which the hydrocarbons and phenol are formed.

The best method of utilizing the tar acids composing the major part of the tar formed by the low temperature carbonization of coals, a matter which concerns the important problem of the economical uses of coals as fuel, will naturally be acquired from the study of the pyrogenic reaction of cresols.

In the experiment, *o*-, *m*-, and *p*-cresols were passed, at the rate of 3.5–4.5 gr. per hour into a glass tube heated to 600°, 650°, and 700° respectively, in a combustion furnace. The temperature of the reaction tube was measured by means of a thermocouple inserted into the tube, and the reaction products—gas and tar, were separately collected in receivers connected by means of a delivery tube to one end of the tube, as may be seen in Fig. 1 mentioned in the experimental part.

The gaseous product was analysed with the Bone-Wheeler gas analysis apparatus, of methane, hydrogen, carbon monoxide, and carbon dioxide. The tar separated from water, was analysed for hydrocarbon, phenols and polymers; the phenol and the cresol which were separated from the hydrocarbons by means of an 8% caustic soda solution, had their content

(1) H. Meyer und A. Hofmann, *Monatsh.*, **38** (1917), 343.
(2) F. Fischer, *Abh. d. Kohle*, **4** (1919), 373; **5** (1920), 413.
(3) E. Müller, *J. prakt. Chem.*, [2] **58** (1898), 1.

estimated by the aid of density with reference to that of a mixture of a known quantity of two phenols.

When 20 gr. of *m*-cresol were passed in 5 hours through a glass tube heated to 600°, a gaseous product was noticed to be produced in the first few minutes, and then followed the tar-formation with diminution of the gas-production in process of time, and only 15.5% of the cresol decomposed, and the product was composed mostly of a polymer of high boiling point with 160 c.c. of gas composed of methane, carbon monoxide, carbon dioxide, and hydrogen. The formation of phenol and hydrocarbons was noticed to increase with the rise of the reaction temperature as will be shown in the Table.

The yield of gaseous substances from *m*-cresol at 650° was very meagre, but increased pari passu with the rate of decomposition of the cresol with the rise of the reaction temperature. The composition of the gas formed at 600° being rich in CO_2 and poor in H_2, is quite different from that generated at 650°, in which hydrogen is predominant, and the content of CO and CH_4 shows but slight variation through the whole range of the reaction temperatures. Phenol and benzene began to appear in a measurable quantity at 650°, and at high reaction temperature the yield of both phenol and benzene increased, viz., the formation of phenol is favourable at a low temperature ; while the production of benzene and carbon monoxide was increased with the rise of the reaction temperature.

From this fact, it will be understood that the formation of phenol and benzene is due to the thermal decomposition of the polymer which is produced as a primary reaction product. As to this polymer, we have many evidences for considering it a mixture of some diphenyl ether derivatives. P. Sabatier[1] has reported that phenols when heated to 400°–500° in the presence of alumina yield chiefly aromatic ethers, and diphenyl ether according to the writer's experiment was decomposed by passing it through a glass tube heated to 700° into water, benzene, phenol, some polymers and carbon, and the gaseous products were composed mainly of carbon monoxide and hydrogen, and an inferior content of methane and carbon dioxide. Similar statements about the decomposition of phenyl ethers under different conditions were previously made by C. Graebe[2] and W. Ipatiew[3].

Taking these facts into account, the thermal decomposition of phenols would be represented in the following schemes :

$$(1)\quad ROH \longrightarrow ROR + H_2O$$

(1) P. Sabatier, "Die Catalyse in der Organischen Chemie" (1927), 281.
(2) C. Graebe, *Ber.* **29** (1896), 1877.
(3) W. Ipatiew, *Ber.* **60** (1927), 1963.

$$(2)\quad ROR \longrightarrow \begin{cases} R' + H_2O \\ ROH + RH \\ \text{polymer} \\ CO,\ H_2,\ CH_4,\ H_2O \text{ and carbon} \end{cases}$$

phenol, for example, is condensed first by splitting off one mol of water from two mols of phenol into phenyl ether which then decomposes into benzene and phenol on the one side, and on the other polymerises into complex compounds and eventually into carbon, liberating such simple substances as water, carbon monoxide, carbon dioxide, hydrogen and methane.

In the thermal decomposition of cresol, besides toluene, benzene and phenol would be produced, as the result of demethylation happening simultaneously with the formation and decomposition of cresylether. The rate of detachment of the methyl group from the cresol molecule is assumed to depend mostly on the relative position of the methyl group visa vis the hydroxyl group.

As a matter of fact, the formation of hydrocarbon and phenol from cresol predominates at low temperatures, while the decomposition of the phenol into hydrocarbon is favorable at high temperatures with the formation of carbon monoxide and water, and the writer has noticed diphenyl occurring in the reaction product.

2. The Comparison of the Thermal Decomposition of *m*-, *o*-, and *p*-Cresols. When *o*- and *p*-cresols were treated at 700° in a glass tube, under conditions similar to those of *m*-cresol, the decomposition of the substances proceeded in a similar manner to the isomeric substance but differing in the proportionate quantities of the reaction products as may be seen in the following Table.

Cresol		*m*	*o*	*p*
Decomposed cresol	%	51.0	88.0	93.5
Benzene hydrocarbon	%	8.0	11.5	13.0
Phenol	%	9.5	22.5	20.0
Polymer	%	17.5	24.5	21.5
Water	%	1.5	3.5	3.0
Gas	c.c./gr.	108	165	150
(Vol. %)	CO	40.5	29.3	36.7
	CH_4	35.8	47.6	45.6
	H_2	23.2	22.2	17.1

The rate of decomposition of the cresols is in the order *p*, *o* and *m*, but the formation of the gaseous products is greatest with the ortho compound and least with the meta, and the para-compound stands between those two.

The proportions of CO, CH_4 and H_2 in the gaseous product from the meta-compound is different from that produced from the ortho and the para-isomers, and this fact will afford some notion of the composition of the liquid products from *m*-cresol, in which hydrocarbons of a low boiling point such as benzene and toluene compose the major part, but phenol is the chief reaction constituent from other cresols. Such a difference in the reaction products from the three isomers of cresol is partly due to the easiness by which the elimination of the methyl group from the cresol molecule will take place according to the position combined the group to the carbon atom of the benzene nucleus.

As a matter of fact, the methyl group situated in ortho or para position to the hydroxyl group in the cresol molecule is easily removed in course of the pyrogenesis of the substances, and consequently the phenol-yield is great in *o*- and *p*-cresols, and it is established that *m*-cresol is the most stable and *p*-cresol the most unstable toward thermal treatment.

3. Effect of the Material of the Reaction Tube. In order to investigate the catalytic effect of the wall-materials of the reaction tube on the thermal decomposition of cresols, porcelain, copper and iron tubes were employed, through which *m*-cresol was passed under similar experimental conditions as described in the experimental part, and the amount of cresol affected by the reaction was greatest with the copper tube; and the effect of the material is in the order: copper, iron, porcelain, and glass; while for the formation of gaseous products, the order is iron, copper, porcelain, and glass.

The gas from *m*-cresol which is passed into an iron tube, is chiefly composed of hydrogen and CO, with a small amount of methane, a result quite different from what happens when glass, porcelain or copper tubes are employed. In the latter three cases the constituents of the gaseous products are similar, the chief constituents being CO and methane, and glass and porcelain seem to affect the cresol catalyticaly as may be assumed from the gaseous constituents, in a similar manner, to the decomposition of cresol. This assumption of the catalytic effect of the tube materials is evidently approved on examination of the liquid reaction products which are composed of benzene hydrocarbon (H.C.) and phenol in the following ratio with the several tubes:

Material of tube		Glass	Porcelain	Copper	Iron
Decomposed cresol	%	41	75.5	92.5	77.5
H.C.		8.0	13.5	20.5	8.5
Phenol		9.5	8.0	5.5	4.5
Cresol changed into gas & carbon	%	14.5	33.5	46.5	53.0
Decomposed *m*-cresol	%	51.0	75.5	92.5	77.5
Benzene hydrocarbon	%	8.0	13.5	20.5	8.5
Phenol	%	9.5	8.0	5.5	4.5
Polymer	%	17.5	18.0	16.5	6.5
Water	%	1.5	2.5	3.5	5.0
Gas	c.c./gr.	108	183	314	342
(Vol. %)	CO	40.5	41.0	43.1	22.1
	CH_4	35.8	34.5	33.5	7.0
	H_2	23.2	22.9	18.3	67.7

The relative amount of the hydrocarbon and phenol in the reaction product is the same whether porcelain or iron tubes be employed, though the copper tube shows a different result. The formation of phenol and the hydrocarbon being attributed to the decomposition of the polymer is supposed to proceed equally in glass or porcelain tubes, according to the following scheme:

$$R\text{-}O\text{-}R \longrightarrow R + ROH$$

but the formation of the hydrocarbon is facilitated with the iron and copper tubes, as may be manifest in the scheme:

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!O \longrightarrow 2R + H_2O$$

When the iron tube was employed the gaseous substances were predominant in the reaction product, which formed at the expense of the polymer, and the latter was partly transformed into the hydrocarbon and phenol.

From these facts it may be concluded that the materials used for the reaction tube will promote catalytically any one of the reactions occurring in the thermal treatment of cresols, and the formation of phenol and polymers from cresols is favoured by the use of a glass or porcelain tube, and the production of benzene is promoted with the use of a copper tube; but with the employment of an iron tube a complete decomposition into gas, water and carbon is accelerated.

4. Effect of Catalysts. The occurrence of benzene, toluene and phenol in the coal tar by the high temperature distillation of coals was attributed in the foregoing paragraph to the fact that the tar acids formed as one of the primary reaction products in the tar generated by the carbonization are cracked to form these substances in passing the heated zone of coke or coal in a retort, which consists of the mineral matter together with some organic substances of complex nature. The thermal decomposition of cresols in the presence of some catalysts which are similar in composition to coal ash is very important in order to learn the mechanism of the reaction of the formation of the light fractions of the tar from coal materials.

There is some resemblance between the composition of some Japanese coal ash and of Japanese acid earth, both containing alumina and silica as a chief constituent as shown in the following Table :[1]

	Shimbara coal ash	Japanese acid earth
SiO_2	59.2	65.19
Al_2O_3	26.2	} 16.36
Fe_2O_3	5.6	
MnO_2	trace	—
CaO	4.8	0.73
MgO	1.2	2.72
Na_2O+K_2O	1.7	0.11

It is, therefore, not inconceivable that the catalytic action of the Japanese acid earth and alumina are analogous to that of coal ash. *o*-Cresol was passed into glass tube which contains Japanese acid earth or alumina, to see the catalytic effect on the decomposition of the substance.

In each case, the formation of a polymer and phenol is evidently favoured at a low temperature, and the yield of benzene hydrocarbon and carbon monoxide is increased with the rise of the reaction temperature due to the cracking of the polymer.

To discover a special feature of the catalysts for the decomposition of the cresol, the reaction products at 700° were studied.

The rate of decomposition of cresol is increased in the presence of the catalysts, and the alumina tends to promote the gasification of the substance. The hydrogen content in the produced gas increased with alumina, due to the expense of methane by the action of water in the presence of the

(1) *Research Report of the Naval Fuel Depot, Japan*, **1** (1926), 40.

catalyst. The decomposition of polymers into hydrocarbons is obviously accelerated in presence of these catalysts, in which some difference was noticed when the liquid product was examined precisely according to the difference in the chemical constituents of the catalysts.

		Blank	Acid earth	Al_2O_3
Changed cresol	%	88.0	91.5	94.0
Benzene hydrocarbon	%	11.5	13.5	13.0
Phenol	%	22.5	16.5	12.5
Polymer	%	24.5	18.5	12.5
Water	%	3.3	5.0	4.0
Gas	c.c./gr.	165	198	327
(Vol. %)	CO	29.3	28.5	22.3
	CH_4	47.6	46.8	33.7
	H_2	22.2	24.0	36.9

5. Effect of Deposited Carbon. In the course of the pyrogenetic reaction of cresols, the writer has noticed that in the first several minutes of the reaction, gaseous substances only are produced, followed by the formation of tar, the nature of the latter substance would not be the same as passing of time of reaction.

These observations led the writer to the notion that in the beginning of the process of pyrogenesis, the complete decomposition of cresols into gaseous compounds and carbon will prevail, and the latter substance accumulated in the reaction tube will retard the gasification, but promote the oxidation or removal of hydrogen from cresols to a polymer which will in turn change into phenol and benzene.

In passing *p*-cresol into the glass tube with alumina at 700°, the main reaction products in the first hour consisted of hydrogen, methane, carbon monoxide and water, with some quantities of carbon and some polymers. The composition of the gaseous products was determined to be

$$CO\ (CO_2),\ 1;\quad CH_4,\ 1.5;\quad H_2,\ 3.8.$$

The formation of these substances is supposed to occur by the reaction represented by the equation which differs slightly from that reported by E. Müller[1]

$$2C_6H_4\begin{matrix}CH_3\\OH\end{matrix} = H_2O + CO + 2CH_4 + 3H_2 + 11C$$

In the latter phase of the reaction, polymers and phenol are the chief reaction product, and their formation will be connected with the deposition of carbon in the reaction tube. The physical and chemical properties of carbon produced by the thermal decomposition of organic compounds, vary with not only the nature of the substance from which the carbon is produced, but the external conditions such as the temperature and the pressure[2] under which the carbonization takes place, also the physical nature of the surface[3] of the tube on which the carbon is precipitated. In fact, some differences have been noticed in the appearance of the carbon deposited on the surface of glass, porcelain, copper and iron tubes, and the difference in composition of the reaction products from cresols is partly due to the physical and chemical nature of the carbon deposited on the tube-walls.

Experimental Part.

Cresols from Kahlbaum, distilled for purification after being treated with anhydrous sodium sulphate, show the following physical constants:

Cresol	B. p.	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$
o-	187.5°—183.3°	1.0426	1.5398
m-	198.5°—199.5°	1.0304	1.5350
p-	197.5°—198.5°	1.0310	1.5335

A reaction tube of 2 cm. in diameter and 1 m. in length, made of glass, porcelain, copper, or iron, was heated in a combustion furnace, and the

(1) E. Müller, loc. cit.
(2) W. J. Mellor, "Comprehensive treaties on inorganic and theoretical chemistry," V, (1924).
(3) K. A. Hofmann und U. Hofmann, *Ber.*, **59** (1926), 2433.

temperature of the inside of the tube was measured by means of a thermocouple; the cresols were gradually dropped into a reaction tube by means of a capillary tube attached to the tube, and the reaction product was collected in a receiver which was cooled with a freezing mixture of ice and salt, and the generated gas which escaped from the receiver was collected on a 10% sulphuric acid solution in a bottle. (Fig. 1).

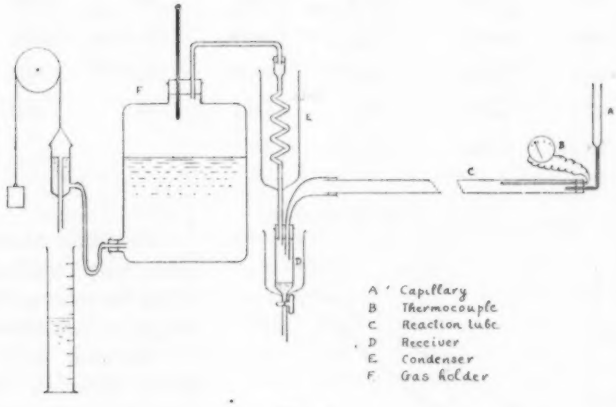

Fig. 1

The gas produced was analysed with a Bone-Wheeler[1] gas analysis apparatus, and the content of CO_2, CO, CH_4 and H_2 specially estimated in each experiment. The tarry matter condensed in the receiver was subjected to fractional distillation after water was separated, into three parts; the first part boiled from 78° to 120°, the second part b.p. 120°–200°, the residue b.p. up 200°, and each fraction was treated with 8% caustic soda solution to separate the phenolic substances from the neutral ones and redistilled. The main fractions were estimated to be composed of the following constituents.

1. The neutral fraction b.p. (79°–120°) benzene and toluene
2. ,, acidic ,, b.p. (178°–200°) phenol and cresols
3. ,, residue ,, b.p. (200° —) polymer

The phenol-content in the acidic fraction (178°–200°) was calculated by weight from its density by consulting the following Table and Fig. 2.

(1) C. Grice and W. Paymann, *Fuel in Science and Practice* (1924), 236.

o-Cresol		*m*-Cresol		*p*-Cresol	
Phenol %	$d_{4°}^{25°}$	Phenol %	$d_{4°}^{25°}$	Phenol %	$d_{4°}^{25°}$
0	1.0426	0	1.0304	0	1.0310
8.4	1.0448	18.6	1.0377	17.7	1.0380
14.9	1.0470	25.9	1.0406	25.4	1.0408
26.4	1.0501	44.7	1.0480	35.9	1.0454
47.8	1.0565	50.2	1.0502	51.7	1.0514
67.7	1.0623	65.4	1.0565	72.7	1.0601
76.7	1 0651	76.7	1.0610		

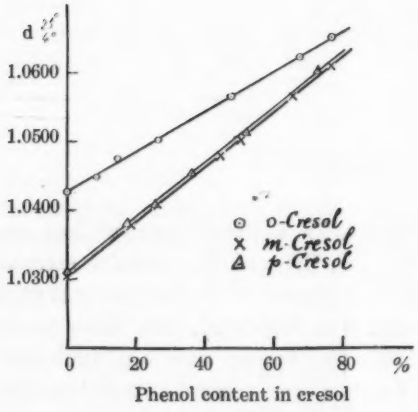

Fig. 2.

The data shown in the Table was obtained by the writer by mixing the known weight of two substances.

Benzene and toluene which occur in the neutral fraction were identified by transforming them into their amino derivatives by the usual method, and also phenol was confirmed by converting into the diazo-derivative.

1. Experiment with a Glass tube. *m*-, *o*- and *p*-cresols were passed at the rate of 3.6–4.2 gr. per hour, into a glass tube heated to 600°, 650° and 700° respectively. At the beginning of the reaction, some gaseous product only was formed, followed by the formation of a liquid substance. The products were analysed and the results are shown in Tables 1, 2 and 3. It was noticed that the inner surface of the tube was covered by a film of carbon, and the higher the reaction temperature the greater the thickness of the carbon film. The appearance of the carbon film is black at 600°, bluish black at 650°, with a grey and dull metallic lustre at 700°.

Table 1.

m-Cresol

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°, 760 mm.	Carbon
600°C.	20.0	4.0	18.7	160	+
650°	20.0	4.0	18.1	620	+
700°	20.0	4.0	17.5	2150	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–)	Water
	gr.	$d_{4°}^{25°}$	$d_{D}^{25°}$	gr.	$d_{4°}^{25°}$	$n_{D}^{25°}$	gr.	gr.
600°	trace	—	—	16.9	1.0307	1.5322	0.9	trace
650°	0.3	—	1.4911	14.9	1.0328	1.5334	1.9	0.2
700°	1.6	0.8672	1.4903	11.7	1.0368	1.5356	3.5	0.3

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	84.5	trace	trace	4.5	trace	—
650°	70.0	1.5	4.5	9.5	1.0	2.1/5.0=0.42
700°	49.0	8.0	9.5	17.5	1.5	11.1/10.6=1.05

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	8	35.6	22.5	36.6	5.2
650°	31	0.9	34.9	42.1	22.1
700°	108	0.5	40.5	35.8	23.2

Table 2.

o-Cresol

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760mm.	Carbon
600°C.	20.0	4.0	18.9	340	+
650°	20.0	3.8	17.5	1560	+
700°	20.0	3.6	15.1	3300	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	$n_D^{25°}$		
600°	0.1	—	1.4892	16.3	1.0444	1.5412	2.0	0.1
650°	1.1	0.8709	1.4964	11.2	1.0495	1.5404	4.0	0.4
700°	2.3	0.8756	1.4946	6.9	1.0615	1.5432	4.9	0.7

(Yield in % for sample)

Reaction temp.	*o*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	76.0	0.5	5.5	10.0	0.5	0.7/ 6.1=0.11
650°	42.5	5.5	13.5	20.0	2.0	7.6/15.8=0.48
700°	12.0	11.5	22.5	24.5	3.5	15.5/25.7=0.62

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	17	2.9	18.6	64.1	14.4
650°	78	2.1	22.5	63.8	11.6
700°	165	0.8	29.3	47.6	22.2

Table 3.

p-Cresol

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760mm.	Carbon
600°C.	20.0	3.8	18.3	410	+
650°	20.0	3.8	15.7	2840	+
700°	20.0	4.2	13.1	3000	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	$n_D^{25°}$		
600°	0.2	—	1.4889	15.5	1.0373	1.5327	1.8	0.1
650°	1.4	0.8691	1.4959	9.4	1.0490	1.5374	3.7	0.5
700°	2.6	0.8711	1.4911	5.4	1.0610	1.5400	4.3	0.6

(Yield in % for sample)

Reaction temp.	*p*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	72.5	1.0	5.0	9.0	0.5	1.3/5.9=0.23
650°	26.0	7.0	21.0	18.5	2.5	9.7/25.8=0.37
700°	6.5	13.0	20.5	21.5	3.0	18.0/23.7=0.76

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	20	1.7	20.3	62.0	16.0
650°	142	0.9	28.4	57.5	13.5
700°	150	0.7	36.7	45.6	17.1

2. Experiment with Porcelain, Copper and Iron Tubes. Three tubes made of porcelain, copper and iron was used instead of the glass tube, in the experiment with *m*-cresol which was carried out under the conditions shown in the Table, and the results are as follows :

Table 4.

(A) Porcelain tube

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760 mm.	Carbon
600°C.	20.0	4.0	17.2	140	+
650°	20.0	3.6	17.0	680	+
700°	20.0	3.6	14.0	3670	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–)	Water
	gr.	$d_4^{25°}$	$n_D^{25°}$	gr.	$d_4^{25°}$	n_D^{25}	gr.	gr.
600°	trace	—	—	14.7	1.0310	1.5330	1.2	0.1
650°	0.5	0.8630	1.4936	13.4	1.0328	1.5353	2 0	0.2
700°	2.7	0.8684	1.4920	6.5	1.0400	1.5366	3.6	0.5

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	72.0	trace	1.5	6.0	0.5	trace/1.7
650°	62.5	2.5	4.5	10.0	1.0	3.5/5.0=0.70
700°	24.5	13.5	8.0	18.0	2.5	18.6/9.4=1.97

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	7	29.8	24.8	40.5	4.9
650°	34	4.2	35.7	37.9	22.2
700°	183	1.7	41.0	34.5	22.9

Table 5.

(B) Copper tube

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c c. at 0°, 760 mm.	Carbon
600°C.	20.0	4.7	18.2	950	a few
650°	20.0	4.0	15.2	3260	a few
700°	20.0	3.8	11.6	6280	a few

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°—) gr.	Water gr.
	gr.	$d_4^{25°}$	$n_D^{25°}$	gr.	$d_4^{25°}$	$n_D^{25°}$		
600°	0.1	—	—	15.8	1.0313	1.5320	1.0	0.1
650°	1.9	0.8694	1.4930	9.4	1.0367	1.5348	2.9	0.6
700°	4.1	0.8704	1.4900	2.6	1.0472	1.5375	3.3	0.7

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	76.5	0.5	2.5	5.0	0.5	0.7/2.6=0.27
650°	39.5	9.5	7.5	14.5	3.0	12.1/8.2=1.48
700°	7.5	20.5	5.5	16.5	3.5	28.5/6.2=4.60

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	43	21.4	37.2	39.8	1.5
650°	163	4.6	40.0	29.8	25.6
700°	314	5.2	43.1	33.5	18.3

Table 6.

(C) Iron tube

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760 mm.	Carbon gr.
600°C	20.0	3.5	12.9	4080	+
650°	20.0	4.0	12.8	5430	2.5
700°	20.0	3.8	10.0	6850	5.0

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	n_D^{25}		
600°	0.4	0.8663	1.4870	10.4	1.0313	1.5328	1.0	0.3
650°	0.4	0.8704	1.4914	9.6	1.0328	1.5334	1.3	0.7
700°	1.7	0.8726	1.4930	5.4	1.0367	1.5350	1.3	1.0

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	50.5	2.0	1.5	5.0	1.5	2.8/1.8=1.56
650°	44.5	2.0	3.5	6.5	3.5	2.8/3.8=0.74
700°	22.5	8.5	4.5	6.5	5.0	11.8/5.3=2.26

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	204	6.2	25.4	11.3	57.1
650°	271	4.9	25.0	4.3	65.9
700°	342	3.2	22.1	7.0	67.7

3. Experiment with Catalysts. Japanese acid earth or alumina was used in the thermal decomposition of *o*-cresol as a catalyst to investigate their effect on the reaction. Commercial Japanese acid earth was washed repeatedly with water, dried at 100° and then heated to 500°, and alumina from the market was used.

In the experiment, 10 grams of the catalysts, thus prepared, were spread to a length of 70 cm. in the glass tube and heated to the desired reaction temperature for one hour in a current of air, and then *o*-cresol was passed at the rate of 3.3–4.2 gr. per hour through the tube. After the reaction, the surface of the catalyst was noticed to be covered with carbon. The experimental result are shown in Tables 7 and 8.

Table 7.

Japanese acid earth

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760 mm.	Carbon
600°C.	20.0	3.4	16.9	970	+
650°	20.0	4.2	16.4	380	+
700°	20.0	4.0	12.9	3970	+

Liquid

Reaction	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°—) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	$n_D^{25°}$		
600°	0.7	0.8787	1.4952	13.3	1.0456	1.5400	2.0	0.6
650°	1.3	0.8732	1.4949	11.6	1.0504	1.5412	2.7	0.6
700°	2.7	0.8748	1.4944	5.0	1.0618	1.5428	3.7	1.0

(Yield in % for sample)

Reaction temp.	*o*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	59.5	3.5	7.0	10.0	3.0	4.9/ 7.9=0.62
650°	42.0	6.5	16.0	13.0	3.0	9.0/18.5=0.49
700°	8.5	13.5	16.5	18.5	5.0	18.7/18.9=0.99

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	48	0.7	11.6	43.3	44.3
650°	19	0.5	15.3	47.4	36.9
700°	198	0.7	28.5	46.8	24.0

Table 8.

Alumina

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°, 760 mm.	Carbon
600°C.	20.0	3.3	13.8	2690	+
650°	20.0	4.0	12.3	2990	+
700°	20.0	4.2	10.2	6530	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°—) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	$n_D^{25°}$		
600°	0.7	0.8760	1.4900	10.2	1.0483	1.5404	1.7	0.8
650°	1.5	0.8743	1.4947	7.2	1.0537	1.5423	2.6	0.8
700°	2.6	0.8750	1.4935	3.7	1.0623	1.5430	2.5	0.8

(Yield in % for sample)

Reaction temp.	*o*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	41.0	3.5	10.0	8.5	4.0	4.5/11.2=0.40
650°	22.0	7.5	14.0	13.0	4.0	10.4/16.3=0.64
700°	6.0	13.0	12.5	12.5	4.0	18.0/14.1=1.28

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	135	3.0	8.6	35.9	52.6
650°	150	7.3	14.9	44.4	33.2
700°	327	7.1	22.3	33.7	36.9

Table 9.

No. of interval	Time hour	Sample passed gr.	Decomposition products	
			Liquid gr.	Gas c.c. at 0°,760 mm.
I	1	10.7	2.8	4690
II	$3\frac{2}{3}$	39.2	32.9	5232
III	$4\frac{1}{2}$	49.1	40.7	4185

Liquid

No. of interval	Fraction	gr.	$d\frac{25°}{4°}$	$n\frac{25°}{D}$
I	Neutral (79°–120°)	0.3	—	1.4881
	Acidic (178°–200°)	0.7	1.0500	1.5377
	Residue (200° ——)	1.2		
	Water	0.6		
II	Neutral (79°–120°)	1.8	0.8677	1.4924
	Acidic (178°–185°)	3.2	1.0608	1.5439
	,, (185°–190°)	2.3	1.0483	1.5375
	,, (190°–195°)	9.8	1.0347	1.5345
	,, (195°–200°)	4.5	1.0330	1.5341
	Residue (200° ——)	4.7		
	Water	0.5		
III	Neutral (79°–120°)	1.9	0.8684	1.4903
	Acidic (178°–185°)	3.0	1.0546	1.5391
	,, (185°–190°)	4.0	1.0462	1.5366
	,, (190°–195°)	13.0	1.0347	1.5356
	,, (195°–200°)	7.8	1.0326	1.5349
	Residue (200° ——)	5.5		
	Water	0.3		

Liquid (% for sample)

No. of interval	*p*-Cresol	Hydrocarbon	Phenol	Polymer	Water
I	3.8	3.8	2.8	11.2	5.6
II	39.0	4.6	11.5	12.0	1.3
III	46.8	3.8	9.8	11.2	0.6

Table 9.—(*continued*).

Gas (composition in vol. %)

No. of interval	CO_2	CO	CH_4	H_2	C_nH_{2n}
I	3.4	10.8	23.6	59.6	2.8
II	3.4	21.2	33.0	39.6	2.6
III	3.1	24.3	39.5	30.1	2.5

4. Experiment on the Effect of the Deposited Carbon. 99 grams of *p*-cresol were passed in 9 hours into a glass tube with three porcelain boats which were situated separately at certain intervals in the tube, each containing about 10 gr. of alumina. The reaction products, gas and tar were collected successively in three intervals; the first one hour, then 3.5 hours for the second fraction, and finally 4.5 hours for the third, and each collection was analysed, and the results are shown in Table 9.

In order to learn the chemical nature of the carbon deposited on the catalyst in the boats, the whole content of these boats was subjected to combustion, and carbon and hydrogen were estimated as in the elemental analysis of an organic compound.

Position in reaction tube	Capillary side	Centre	Receiver side
C %	97.3	95.3	92.5
H %	2.0	3.1	3.1
O %	0.7	1.6	4.4
C/H	4.05/1	2.56/1	2.48/1

As will be seen from the above Table, the so-called carbon deposited on alumina is mostly composed of carbon, and its composition varies with the position in which the boat is situated in the tube. When cresol comes into contact with the heated surface of alumina, it would undergo repeated polymerisations and decompositions, splitting off oxygen and hydrogen, and producing such a carbon-rich substance as the so-called carbon[1].

5. Diphenyl Ether. Diphenyl ether prepared from chlorobenzene and sodium phenolate, showed b.p.$=(97.5°–98.5°)_{3mm.}$, $d_{4°}^{25°}=1.0716$, $n_D^{25°}=1.5782$, was passed into a glass tube heated to 700°, at the rate of 15.4 gr. per hour, and thus, 30.8 gr. of diphenyl ether yielded 27.0 gr. of the tarry substance, 0.3 gr. of water, 1900 c.c. of gas and some carbon. Analytical results of the tar are shown in the following Table.

(1) M. Berthelot, "Essai de mecanique chimique", II, (1879), 137.

The neutral fraction.

Fraction	gr.	%		
1. 78°–100°	3.5	11.4	$d_{4°}^{25°}=0.8753$, $n_D^{25°}=1.4974$	benzene (24.7 mol %)
2. 220°–260°	5.8	18.8	$d_{4°}^{25°}=1.0734$, $n_D^{25°}=1.5958$	mainly diphenyl ether
3. 260°–330°	1.9	6.2		,, diphenylene oxide
4. residue	3.6	11.8		

The acidic fraction.

Fraction	gr.	%		
1. 178°–185°	4.1	13.3	m.p. [39.5°–40.5°]	phenol (34.1 mol %)
2. 280°–290°	0.4	1.3		
3. residue	0.2	0.6		

Benzene in the neutral fraction was confirmed by the usual chemical method. The fraction b.p. 220°–260° of the neutral part was assumed to be a mixture of diphenyl ether and diphenyl from the physical constants. From the fraction b.p. 260°–330° of the neutral part, a substance of m.p. 80°–81° by recrystallisation from alcohol was isolated, which was identified as diphenylene oxide by converting it into picrate with a m.p. of 96°–97°.

The composition of the gas was determined and shown by volume.

CO	H_2	CH_4	C_nH_{2m}	C_2H_4	CO_2
51.9	38.9	7.6	0.7	0.4	0.5

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